A PSEUDOVECTOR NUCLEAR HYPERFINE INTERACTION*

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In many studies of nuclear hyperfine interactions in polyatomic molecules and solids it has been assumed that the electron spin $\boldsymbol{S}$ and nuclear spin $\boldsymbol{I}$ are coupled through a symmetric dyadic $\mathfrak{S}$, corresponding to a hyperfine spin Hamiltonian,

$$\mathfrak{H}_{hf} = \boldsymbol{S}\cdot\mathfrak{S}\cdot\boldsymbol{I}\cdot \tag{1}$$

When $\mathfrak{S}$ is referred to a set of principal axes x, y, z, $\mathfrak{H}_{hf}$ takes the familiar form,

$$\mathfrak{H}_{hf} = \mathfrak{S}_{xx}S_xI_x + \mathfrak{S}_{yy}S_yI_y + \mathfrak{S}_{zz}S_zI_z\cdot \tag{2}$$

The purpose of the present brief note is to describe an extremely simple model that illustrates the necessity of generalizing (1) to include a pseudovector hyperfine coupling:

$$\mathfrak{H}_{hf} = \boldsymbol{S}\cdot\mathfrak{S}\cdot\boldsymbol{I} + \boldsymbol{V}\cdot(\boldsymbol{S}\times\boldsymbol{I}). \tag{3}$$

In equation (3), $\boldsymbol{V}$ is a pseudovector fixed in the molecule or ionic complex.

The Model.—Consider a molecule containing a paramagnetic metal ion P and a magnetic nucleus X located in some other atom. For simplicity, let the molecular framework about P have an n-fold axis of symmetry that passes through P, where $n \geqslant 3$. This symmetry axis is parallel to the unit vector $\boldsymbol{\kappa}$ in Figure 1. The vector $\boldsymbol{r}$ is drawn from P to X, and the direction of $\boldsymbol{\kappa}$ is defined so that $\boldsymbol{\kappa}\cdot\boldsymbol{r} = r\cos\chi$ is positive. The unit vector $\boldsymbol{h}$ is defined by the equation $\boldsymbol{r} = \boldsymbol{\kappa}r\cos\chi + \boldsymbol{h}r\sin\chi$. In general, the Zeeman spin Hamiltonian for the coupling of an electronic spin of a paramagnetic ion to a uniform field $\boldsymbol{H}$ is [1]

$$\mathfrak{H} = |\beta|\boldsymbol{S}\cdot\boldsymbol{g}\cdot\boldsymbol{H}, \tag{4}$$

where the spectroscopic splitting $\boldsymbol{g}$ dyadic is

$$\boldsymbol{g} = \boldsymbol{\kappa\kappa}g_{\parallel} + (\boldsymbol{hh} + \boldsymbol{\omega\omega})g_{\perp} \tag{5}$$

and where $\boldsymbol{\omega} = \boldsymbol{\kappa}\times\boldsymbol{h}$. Assume the ion P to be far enough away from X that the field at P due to the nuclear magnetic moment $\gamma\hbar\boldsymbol{I}$ is uniform over the effective volume of P. The field at P due to the nuclear moment is

$$\boldsymbol{H}_{\mathrm{I}} = \gamma\hbar\boldsymbol{T}\cdot\boldsymbol{I}, \tag{6}$$

$$\boldsymbol{T} = \frac{1}{r^3}\,[3\boldsymbol{rr}/r^2 - \boldsymbol{U}] \tag{7}$$

and where $\boldsymbol{U}$ is the unit dyadic. From equations (4) and (6) we obtain the hyperfine spin Hamiltonian,

$$\mathfrak{H}_{hf} = |\beta|\,\gamma\hbar\boldsymbol{S}\cdot\boldsymbol{g}\cdot\boldsymbol{T}\cdot\boldsymbol{I}. \tag{8}$$

The dyadic $|\beta|\,\gamma\hbar\boldsymbol{g}\cdot\boldsymbol{T}$ is not symmetric but can be written as the sum of symmetric and skew symmetric dyadics:

$$|\beta|\,\gamma\hbar\mathbf{g},\ \mathbf{T} = \mathfrak{S} + \mathbf{E}. \tag{9}$$

For the problem at hand,

$$\mathbf{E} = \frac{3}{2}\,\gamma\hbar|\beta|\,\frac{1}{r^3}\,(g_{\parallel} - g_{\perp})(\cos\chi\sin\chi)(\boldsymbol{\kappa}\mathbf{h} - \mathbf{h}\boldsymbol{\kappa}). \tag{10}$$

The hyperfine coupling via the skew symmetric dyadic can also be written as the scalar product of two pseudovectors,

$$\mathfrak{S}\cdot\mathbf{E}\cdot\mathbf{I} = \mathbf{V}\cdot(\mathbf{S}\times\mathbf{I}), \tag{11}$$

where

$$\mathbf{V} = \frac{3}{2}\,\boldsymbol{\omega}\gamma\hbar|\beta|\,\frac{1}{r^3}\,(g_{\parallel} - g_{\perp})\cos\chi\sin\chi.$$

Therefore equation (3) rather than Equation (1) is the general form for the spin Hamiltonian when $g_{\parallel} \neq g_{\perp}$, ane $\chi \neq 0, \pi/2$.

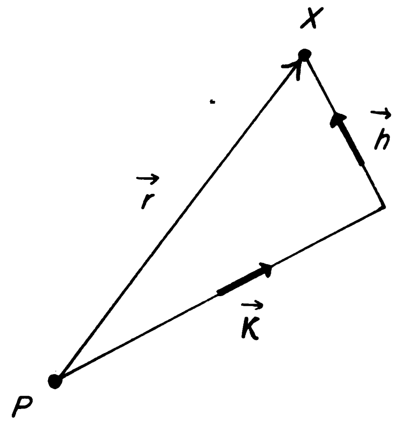

FIG. 1.—Pseudovector coupling between an electron spin situated at P and a nuclear spin at X.

Remarks.—In classical terms, the symmetrical dyadic interaction (1) or (2) is one which tends to orient the spins **S** and **I** parallel or antiparallel to one another, and along x, y, or z, depending on whether $\mathfrak{S}_{xx}$, $\mathfrak{S}_{yy}$, or $\mathfrak{S}_{zz}$ is the largest. On the other hand, the pseudovector coupling (11) is one which tends to orient the spins **S** and **I** perpendicular to one another and to keep both spins in the plane of $\boldsymbol{\kappa}$ and $\mathbf{h}$ in Figure 1. The pseudovector contribution to the hyperfine interaction can produce *first-order* effects on the hyperfine structure of paramagnetic resonance spectra. In fact, for certain parameters of our model, $3\cos^2\chi - 1 = 0$ and $g_{\perp} = 0$, the asymmetric nature of the coupling is dominant; i.e., the only coupling is between S_{κ} and I_h. Comparable effects may also exist and be observable for electron-electron spin coupling.

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[1] M. H. L. Pryce, *Proc. Phys. Soc.* A, **63**, 25, 1950.